

**Rough English translation**

**WO9523024A1 1995-08-31 METHOD OF MANUFACTURING POROUS COMPONENTS WITH A CATALYTIC ACTIONS (en) - Abstract**  
**English Abstract:**

Described is a method of manufacturing porous, gas-permeable, catalytically active components (10) with internal surfaces (15) for the catalysis of chemical reactions. A carrier (12) is impregnated at the surface or in the main body of the carrier with catalytic material (13, 14), in particular a noble metal or a getter material such as an alkaline-earth oxide. The impregnated carrier (12) is then sintered with a ceramic substrate material, the carrier (12) being removed by evaporation. The catalytic material (13, 14) remains behind on the pore walls. A catalytically active protective layer (10) produced in this way is suitable for use in automobile exhaust-gas sensors.

**- Bibliographic Data**

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Advanced20051008 (A I R M EP)

**-Patent References Cited-Backward:**

**Retrieved Selected**

□	Publication Number	Publication Date	Title	Applicant/Assignee	Cited By
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□	DE4131503A1	1993-04-01	Abgassensor und Verfahren zu dessen Herstellung.	Robert Bosch GmbH	Originates from the search report (A)
□	EP0444495A1				Originates from the search report (A)
□	DE4215481A1	1993-11-18	Geformter keramischer Katalysator und Verfahren zu seiner Herstellung.	Siemens AG	Originates from the search report (A)
□	DE2210438A1	1973-09-06	HOCHPOROESER UND GASDURCHLAESSIGER KERAMISCHER TRAEGER, INSBESONDERE FUER KATALYSATOREN UND VERFAHREN ZU SEINER HERSTELLUNG	SIEMENS AG, 1000 BERLIN U. 8000 MUENCHEN	Originates from the search report (A)
□	EP0148622A2				Originates from the search report (A)

▼ **Description**

**English Description:**

Proceed? .n to the production porous-divide with katalytischer function state of the art the invention concerns a procedure for the production more porously, more gaspermeable, katalyti-@isch effective parts in accordance with the kind of the principal claim.

From the DE--OS 41 31 503 is well-known it, porous, gaspermeable, ceramic parts, to manufacture for example thin layers with catalytic materials for gas sensors. Porous parts are among other things filters, frits, diaphragms, sponges and capillaries or channels exhibiting bodies. As catalytically active materials precious metals and/or precious metal alloys are mentioned. The use of oxides beside metals in only one ceramic(s) part or also in together-bordering spatially ranges from ceramic(s) parts with

in each case a catalytic means are descriptive.

During sintering of mixtures of catalytically active materials with ceramic(s) powders the catalytic means are full-enclosed mostly by ceramic(s), whereby a high materials consumption becomes necessary for the acquisition of sufficient catalytic activity. To bringing catalytic materials into porous ceramic parts by impregnation with a salt; Öffnung ceramic(s) with means, which coin/shape the cavity form and which attitude to porosity permit, is sintered, impregnated and again heated up. An even distribution of the catalytic means after thermal distance of the form-forming means on the internal surface of the ceramic, permeable part is not always reached thereby satisfying. Usable surface on the inside of the ceramic part lies katalytisch ineffectively fallow.

Usually Thermalruß, graphite, Theobromin, - Indigo, Indanthren " - Polylethylen-Epoxid-Wachse and Piccin as, form-coining/shaping means are used. Parts with fixed measures and forms, which can be manufactured, the selection (EP-A 0,148,622).

Task of the invention is it, using form-forming means figuration regret, porous, permeable parts on surfaces on the inside with even over this internal surface distributed catalytically active means to coat.

Form-coining/shaping means, whose surface catalytic means exhibit and which are suitable for automatable production, are a further article. the invention.

The task of the invention will solved by in the principal claim the given muddled. A form screen end a means, which is a thermally decomposable, burn outable and/or evaporatable material, makes possible here, to apply on the internal surfaces of the part catalytic materials. The range of the catalytic means in the part, thus specified, increases its effective surface for the purpose of the catalysis.

Because of the higher catalytically effective surface the materials consumption of the catalytic means and the form-coining/shaping means can be reduced with same catalytic effectiveness. A reduction of the catalytically effective part is possible and the mass decrease of the part extends the mobile employment. By the better uniform distribution of the catalytic material a clear improvement of the life span of the part enters. with large form-coining/shaping with ILein it is possible, coherent internal Oberfläche "cl@.enbereiche of the part with catalytic material zÜi covers. Regarding the production of the part.

the procedure is needed simplified, as no impregnation is more necessary for bringing in the catalytic means, the one thermal subsequent treatment.

If two or i become (teach different catalytic means used, then it is possible to develop under utilization of the architecture of a form-coining/shaping by means of with the catalytic means a catalyst at the internal surfaces of the part with that the catalytic means in a firm spatial relationship to each other. In addition different density gradients of mixtures of the catalytic means are adjustable. It is no more problem to manufacture a catalyst on the internal surfaces of the part, composed of several layers.

From the characteristics indicated in the Unteransprüchen further advantages result.

By applying the catalytically effective means on the surface of the form-coining/shaping means connected ranges or samples can be provided with catalytic material on the internal surfaces of the part.

It is to be adapted by different catalytically effective means on the surface of the form-coining/shaping means possible catalytic means unterschiedli.chen chemical reaction conditions. Around for example CO, HCl NO, and O<sub>2</sub> in automobile exhaust gases into the thermodynamic equilibrium to convert are, preferably RH-catalysts with deep, Pt-catalysts at high temperatures next to each other effectively. By - the coating according to invention, a separation of catalytic means is possible, which will mix sich-anderfalls and by it their effect to lose. An alloy formation of Pt M-@@.t RH can be avoided in such a way.

In particular for that, case that the powder grains exhibit approximately spherical shape, becomes a particularly favorable relationship of surface: Volume at firm pore radius for the catalysis usable. Furthermore the permeability of the part with well-known dimensions can be stopped purposefully by the choice of the dimensions of form-coining/shaping means and with catalytic means provided form-coining/shaping means.

With procedure according to invention is possible it to bind the catalytic means in a simple manner to the form-coining/shaping means.

An additive from Theobromin to thick-film pastes and/or.

ceramic molding materials of the basic substance of the part, during sintering sublimates and defined cavities leaves is suitable excellently for the automated screen printing technology.

Design the figure shows one @,--hnitt by a porous part with catalytically effective -'. @-schichtungen on the pore surfaces.

Description of the remark examples figure 1 shows schematically a porous part 10, which is manufactured in the procedure according to invention. The channel 16 grew together from closed-up pores 12, whose internal surfaces exhibit 15 kataivt.ische means 13 and/or 14. Furthermore is insulating, for example spherical, catalytically ineffective pore 17 in the part 10 represented. The porous part of 10 is from zirconium dioxide ceramic(s), the catalytic means 13 is a getter or a getter, preferably from oxides, preferably from alkaline earth metal oxides, and the catalytic means 1A2 is a precious metal, an in particular platinum or a rhodium. A gas ii, for example the exhaust gas of a thermal engine, flows from the surface of the permeablen part of 10 into the channel 16 to the back of the part of 10 and withdraws there. Isolate lying pores are isolated recognizably.

The form-coining/shaping means will become with chemical Fällprozessen, coated by

dead separating on Pulverteilchen, by vaporizing Pulverteilchen, by laser-induced decomposition of gases on Pulverteilchen or in the fluid bed with types of dust on the Pulverteilchen with catalytic means 13 14 or these catalytic means brought into the volume of the form-coining/shaping means. The subsequent treatment of a catalytic platinum layer for the increase of the adhesive strength on Picein took place favourably in the mitrogen-hydrogen mixture stream with 900 degrees Celsius, for rhodium as catalytic means is 1000 degrees Celsius more favourably.

As mitrogen-hydrogen mixture a mixture of 10 parts hydrogen and 90 parts nitrogen was used.

To the production of the part! 'v are mixed, agitated or sprayed powders, which form the material of the part of 10, with powders of form-coining/shaping means, which unites catalytic means 13, 14 to exhibit, preferably and sintered afterwards.

Sintertemperatur-der mixture lies between 500 and 1600 degrees Celsius zirconium dioxide ci more llver with Piceinpulver of firm grain size of  $D = 4$  micrometers. The contraction of the part of 10 leads to a diameter of the pores, which is smaller than the urpÜngliche grain diameters of the form-coining/shaping means with catalytic means. As form-coining/shaping means with platinum recompensed Picein, with rhodium recompensed Theobromin or with larger form-coining/shaping grains platinum beside rhodium are preferably used. There is also grains with partial coating one or several catalytic means secondary or one on the other applicable. The different particle size and - form is visible in figure 1. It is as a modification also conceivably, getter substances, for example LiAlO<sub>2</sub>, to begin in place of catalytically active substances.

Example 1 for the production of a porous ceramic(s) part of 10 will grind a Thermalrußpulver with a grain size of 1 to 150 micrometers grain diameter with a zirconium dioxide powder, which contains weight percentage Yttriumoxid up to 5, with an organic binder and with a softener under additive of a solvent. After sintering with 1600 degrees of porosities Celsius one receives e. '---... Ceramic(s) part. Alternatively Indigo, P'L are.i-@gesetzt " -, @@in, Polv-@ l@ylenwachs or Theobromin as formprÄgenz'le means -.

Example 2 for the production of a porous ceramic(s) part of 10 with catalytically effective substances is descriptive used a powder as into example 1, after it was coated preceding with platinum. The form-coining/shaping means is recompensed at its surface by chemical FÄllprozesse, in particular reduction of metallic salt solutions, which lead to the separation vori catalytically effective platinum or rhodium.

Example 3 the grain diameters of the Piceinpulvers, the Theobrominpulvers and the catalytically ineffective form-coining/shaping powder are of various sizes selected for vote to the targeted application.

Example 4 a powder substance from Theobrominpulver with platinum layer - and zirconium dioxide powder is over-laminated and sintered by a powder substance from

Piceinpulver with rhodium layer and zirconium dioxide powder.

Example 5 for the production of a rectangular channel of 100 micrometers channel height is printed 165 micrometers thick and 165 micrometers a broad layer from paste on a ceramic substrate and considered by the more largely selected measures the contraction. The paste was descriptive manufactured as in example 1 and 2, however no zirconium dioxide and Yttriumoxid were used. The received pasty mass is imprinted by means of a usual one of automated silk-screen printing, for example Tamponprint, on a ceramic substrate. After applying a ceramic resist coating this resist coating in the nitrogen stream is strengthened with 900 degrees Celsius. In a following fuel step at air or in oxidizing atmosphere the form-coining/shaping means are arrears-free burned out. Sintering follows with 1600 degrees Celsius.

For the examples specified above it proved as favourable for the Porengröße at the most to the 0 kindles itself value of the layer thickness of the ceramic(s) part which can be manufactured to select, which corresponded to a range of application of 2 to 15 micrometers. The layer thickness of the applied catalytically effective material on the Formpräger was particularly favourable, if the diameter of the form-coining/shaping grains constituted the tenfold value of the layer thickness of a schichtförmigen catalytic substance. By the grain size of the form-coining/shaping means before definable by means of seven the porosity of the part of 10 becomes definable regarding partial density, permeability and the diameter of the pores. As form-coining/shaping means for ceramic(s) parts are usable dust, suspensions, pastes, granulates, fixed particles or prefabricated volume parts for ceramic(s) partial production,

#### ▼ Claims

**Number of Claims: 10**

#### **ENGLISH CLAIMS:**

1 procedure for the production more porously, more gaspermeabler, catalytically effective parts (10) with internal surfaces (15) to the catalysis of chemical reactions of or with gases (11) or as getter (13), with form-coining/shaping means (12) for the inside surface (15), which at the manufactured part (10) far away are characterized, by it that the form-coining/shaping means (12) exhibit catalytic means (13, 14), which after the burning out and/or evaporation of the form-coining/shaping means (12) in the pores of the part (10) remain.

2 procedures according to requirement 1, by characterized that form-coining/shaping means on their surface with onecatalytically effective means (13, 14) are coated, which after the thermal distance of the form-coining/shaping means on upper swearing on the inside (15) of the finished parts (10) arrived.

3 procedure according to requirement 1 or 2, by characterized that the assigned individual form-coining/shaping means different catalytic means (13, 14) on the surface (15) exhibits.

4 procedures according to requirement 1 or 2, characterized by the use of a mixture of form-coining/shaping grains (12), the different Katalysators-substanzen (13, 14), in particular Pt and/or Rh exhibit.

5 procedures according to requirement 1, by characterized that as form-coining/shaping means a powder with essentially spherical grains one uses, whose middle grain diameters smaller than the 0,2-fache smallest measure of a schichtförmigen part (10) is.

6 procedures according to requirement 1 or 2, by characterized that the catalytic means (13, 14) is applied as layer on the form-forming grain, whereby the layer thickness is at the most the 0,1-fache of the grain diameters.

7 procedures after one the Ansprüchen 1 to 6, by characterized that the form-coining/shaping means is a powder, whose grains are coated by chemical precipitation or dead separation or Bedampfung from the gaseous phase.

8 procedures according to requirement 7, by characterized that the catalytic coating (13, 14) on the form-forming grains of a thermal subsequent treatment (sinters) it is submitted for the increase of the adhesive strength of the coating.

9 form-coining/shaping means for the procedure according to requirement 1, by characterized that powders from Picein, Thermalruß, Theobromin, Indigo, polyethylene or mixtures of these materials are used.

10 catalytic means for proceed in accordance with requirement 1, characterized by the use of active metals or alloys, in particular from Rh, Pd and Pt, and/or Gettermaterialien from alkaline-earth oxides or mixed oxides  $MIN_2$ , whereby M, N of metals, in particular LiAlO<sub>2</sub>, are.